THE NOXSO CLEAN COAL PROJECT

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ABSTRACT

The NOXSO Clean Coal Project will consist of designing, constructing, and operating a commercial-scale flue-gas cleanup system utilizing the NOXSO Process. The process is a waste-free, dry, post-combustion flue-gas treatment technology which uses a regenerable sorbent to simultaneously adsorb sulfur dioxide (SO₂) and nitrogen oxides (NO_x) from flue gas from coal-fired boilers. The NOXSO plant will be constructed at Alcoa Generating Corporation's (AGC) Warrick Power Plant near Evansville, Indiana and will treat all the flue gas from the 150-MW Unit 2 boiler. The NOXSO plant is being designed to remove 98% of the SO₂ and 75% of the NO_x when the boiler is fired with 3.4 weight percent sulfur, southern-Indiana coal. The NOXSO plant by-product will be elemental sulfur.

The elemental sulfur will be shipped to Olin Corporation's Charleston, Tennessee facility for additional processing. As part of the project, a liquid SO_2 plant has been constructed at this facility to convert the sulfur into liquid SO_2 . The project utilizes a unique burn-in-oxygen process in which the elemental sulfur is oxidized to SO_2 in a stream of compressed oxygen. The SO_2 vapor will then be cooled and condensed. The burn-in-oxygen process is simpler and more environmentally friendly than conventional technologies. The liquid SO_2 plant produces 99.99% pure SO_2 for use at Olin's facilities.

The \$82.8 million project is co-funded by the U.S. Department of Energy (DOE) under Round III of the Clean Coal Technology program. The DOE manages the project through the Pittsburgh Energy Technology Center (PETC).

I. INTRODUCTION

The NOXSO Process is a waste-free, dry, post-combustion flue-gas cleanup technology which uses a regenerable sorbent to simultaneously adsorb SO_2 and NO_x from flue gas from coal-fired utility and industrial boilers. In the process, the SO_2 is converted to a saleable sulfur by-product (liquid SO_2 ,

elemental sulfur, or sulfuric acid) and the NO_x is converted to nitrogen and oxygen. Since SO_2 and NO_x removal occur at normal flue-gas temperatures (downstream of the combustion air preheater), the NOXSO Process is equally suited for retrofit as well as new installations.

Process development began in 1979 with laboratory-scale tests and progressed to pre-pilot-scale tests (3/4-MW) and a life-cycle test. Each of these test programs [1,2,3] has provided data necessary for the process design. Tests of the NO_x recycle concept, which is inherent to the NOXSO Process, have been conducted on small boilers at PETC and at the Babcock & Wilcox (B&W) Research Center in Alliance, Ohio [4].

A 5-MW Proof-of-Concept (POC) pilot-plant test at Ohio Edison's Toronto Plant in Toronto, Ohio, was completed in 1993 [5]. Based on more than 7,000 hours of operation with flue gas, it was demonstrated the process can economically remove more than 95% of the acid rain precursor gases from the flue-gas stream.

The NOXSO Clean Coal Project is the final step in commercialization of the technology. The project was selected during Round III of the DOE Clean Coal Technology Program and is managed through PETC. NOXSO Corporation is the project participant, project manager and technology supplier. The project is being hosted by AGC at their Warrick Power Plant (WPP) near Evansville, Indiana. Morrison Knudsen Corporation is providing engineering services. Projex Inc. is managing construction of the facility.

Final processing of the sulfur by-product to make liquid SO₂ will be completed at Olin Corporation's Charleston, Tennessee facility. The SO₂ plant which utilizes a unique burn-in-oxygen process for converting sulfur to liquid SO₂ is complete. The burn-in-oxygen process is simpler and more environmentally friendly than conventional technologies. Midwest Technical, Inc. provided engineering services. Projex, Inc. managed construction of the facility.

Design and procurement activities are currently being conducted for the NOXSO plant. Preliminary construction activities were completed during the fall of 1996, with full-scale construction scheduled to begin in February 1997. Mechanical completion will occur in June 1998. After commissioning and start-up, the plant will be operated for two years as part of the Clean Coal Project.

Meanwhile, mechanical completion, testing and start-up of the liquid SO_2 plant was achieved in December 1997. Feedstock sulfur will be purchased on the market until the start-up of the NOXSO plant, at which time the NOXSO plant will be the sole source of feedstock for the liquid SO_2 plant. Operating and environmental data will be collected during the plant's operation.

Funding for the \$82.8 million project will be provided by the DOE, NOXSO, AGC, Warrick County, the Southern Indiana Gas and Electric Company (SIGECO), the Gas Research Institute (GRI), W.R. Grace, and the Electric Power Research Institute (EPRI). NOXSO will raise most of its project funds through the sale of revenue bonds issued and guaranteed by the state of Indiana. The guarantee is made possible by state legislation signed into law on March 28, 1995. NOXSO will repay the bonds from revenue generated by the sale of SO₂ allowances and by the sale of liquid SO₂ to Olin during a thirteen-year time period which includes the two-year demonstration operation period.

II. THE NOXSO COMMERCIAL DEMONSTRATION PLANT

The objective of the NOXSO Clean Coal Technology Project is to design, construct, and operate a

NOXSO plant at commercial scale. At the completion of this project, the performance, operability, reliability, construction cost, and operating cost data will be available to assist utilities in making decisions regarding the choice of flue-gas cleanup technology.

Host Site Information

The WPP is owned by AGC and operated by the Southern Indiana Gas and Electric Company (SIGECO). The plant supplies electricity to Alcoa's adjacent Warrick Operations aluminum facility and to the utility grid. The WPP consists of three coal-fired steam electric generating units (Units 1, 2, and 3), each rated at 150 MW, and Unit 4, rated at 300 MW. Unit 4 is jointly owned by AGC and SIGECO. Approximately 80% of the electric power generated at WPP is used by Warrick Operations with the remainder being sent to the utility grid.

As shown in Figure 1, the WPP is located in Warrick County, about 15 miles east of Evansville, Indiana, on Indiana Route 66. The WPP and Warrick Operations are located on approximately 600 acres of land between Indiana Route 66 and the Ohio River.

High sulfur Squaw Creek coal with composition as shown in Table 1 will be burned in Unit 2 after the NOXSO plant is installed. Squaw Creek coal is currently blended with a low sulfur coal for use in Units 1, 2, and 3 to satisfy the Warrick County State Implementation Plan (SIP) limit of 5.11 pounds SO₂ per million Btu of heat input.

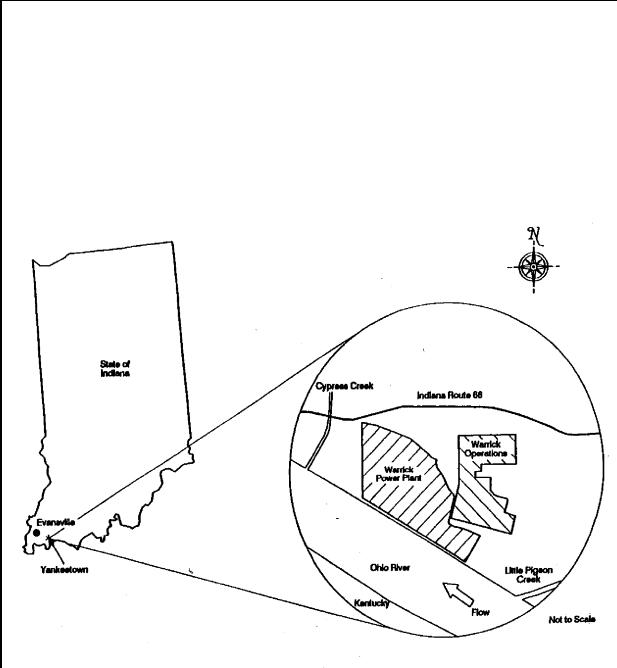


Figure 1. Warrick Power Plant and Warrick Operations Site Location

Parameter	Weight Percent (%)
Moisture	12.92
Carbon	62.02
Hydrogen	4.58
Nitrogen	1.22
Chlorine	0.05
Sulfur	3.39
Ash	8.23
Oxygen	7.60
Higher Heating Value (HHV) (Btu/lb)	11,307

Table 1. Squaw Creek Coal - Ultimate Analysis

AGC has opted-in WPP Units 1, 2, and 3 to the Acid Rain Program of the Clean Air Act (CAA) Amendments of 1990. The Opt-In Program (40 CFR Part 72) allows nonaffected sources, such as AGC's WPP Units 1, 2, and 3, to enter the SO_2 portion of the acid rain program and receive SO_2 emission allowances.

Table 2 shows the design parameters for Unit 2. The wall-fired unit built by Babcock & Wilcox Company (B&W) was placed into service in 1964. The boiler is a natural circulation, Carolina-type radiant unit with 16 circular coal burners arranged in a 4-by-4 grid on a single furnace wall. Coal is reduced from 3/4 inches (in) to 60% less than 200 mesh by B&W EL-76 ball and race pulverizers.

Boiler Manufacturer	Babcock & Wilcox
Operation Date	1964
Primary Fuel	Coal
Start-up Fuel	Natural gas with co-fire
Boiler Type	Wall-fired, natural circulation, Carolina-type radiant unit
Nameplate Rate	144 MW
Steam Flow	1,000,000 lb/hr
Steam Temperature	1,005°F
Design Pressure	1,975 psig
Turbine/Generator Set	160 MW
Existing Burners	16 wall-fired burners
Particulate Control	Western Precipitator electrostatic precipitator designed for 1.83 grains/acfm outlet dust for 688,600 acfm flue gas at 710°F

Table 2. Unit 2 Design Parameters

NOXSO Process Description

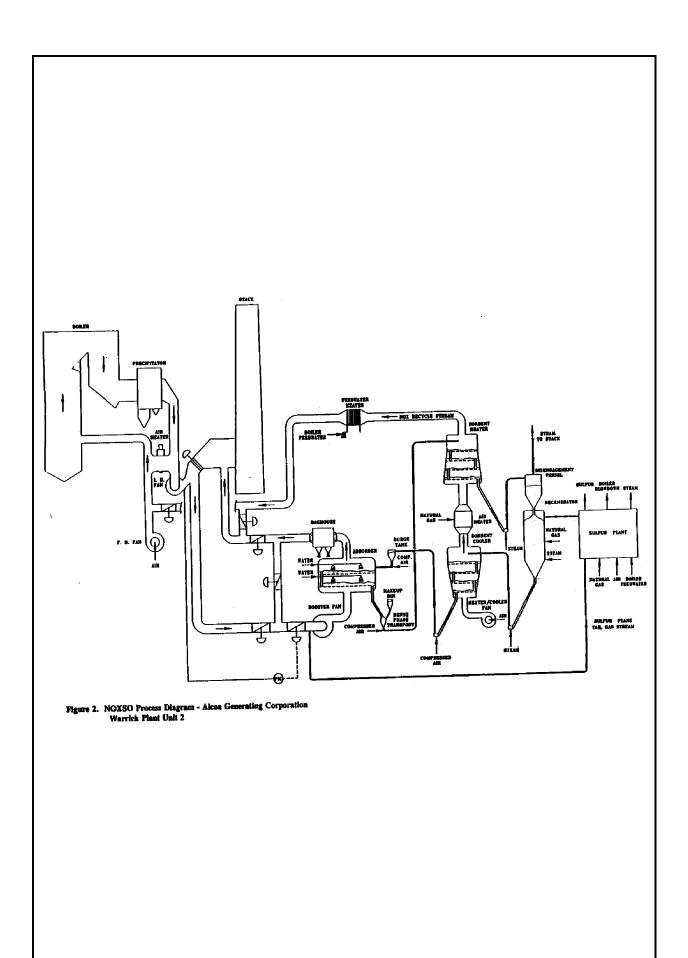
The NOXSO Process is a dry, post-combustion flue-gas treatment technology which will use a regenerable sorbent to simultaneously adsorb SO_2 and NO_x from the flue gas from Unit 2 of AGC's WPP. In the process, the SO_2 will be converted to liquid SO_2 and the NO_x will be reduced to nitrogen and oxygen. The NOXSO plant is designed to remove 98% of the SO_2 and 75% of the NO_x . Details of the NOXSO Process are described with the aid of Figure 2.

Flue gas from the power plant is drawn through two flue-gas booster fans which force the air through two fluid-bed adsorbers and a baghouse before passing to the power plant stack. For simplicity, only one adsorption train is shown in Figure 2. Water is sprayed directly into the adsorber fluid beds as required to lower the temperature to $250\text{-}275\,^{\circ}\text{F}$ by evaporative cooling. The fluid-bed adsorber contains active NOXSO sorbent. The NOXSO sorbent is a 1.2 mm diameter stabilized γ -alumina bead impregnated with sodium. The baghouse removes sorbent which may be entrained in the flue gas and directs it to the fly ash sluicing system.

Spent sorbent from the adsorbers flows into a dense-phase conveying system which lifts the sorbent to the top bed of the sorbent heater vessel. The sorbent flows through the four-stage fluidized-bed sorbent heater in counterflow to the heating gas which heats the sorbent to the regeneration temperature of approximately 1150°F.

In heating the sorbent, the NO_x is driven off and carried to the power plant boiler in the NO_x recycle stream. The NO_x recycle stream is cooled from approximately $360^{\circ}F$ to $140^{\circ}F$ in the feedwater heater. This heat-exchanger heats a slip stream of the power plant's feedwater, thereby reducing the amount of extraction steam taken from the low pressure turbine, enabling the generation of additional electricity. The cooled NO_x recycle stream replaces a portion of the combustion air. The presence of NO_x in the combustion air suppresses the formation of NO_x in the boiler resulting in a net destruction of NO_x .

The heated sorbent is transported through an L-valve to the steam disengaging vessel. Transport steam is separated from the sorbent to reduce the volume of the regenerator off-gas stream. Sorbent gravity flows into the regenerator where it is contacted with natural gas. Through a series of chemical reactions, the sulfur on the sorbent combines with the methane and forms SO_2 and H_2S . Additional regeneration occurs in the steam treater section of the regenerator when the



sorbent is contacted with steam, converting the remaining sulfur on the sorbent to H_2S . The regenerator off-gas stream is directed to a sulfur recovery plant where the H_2S and SO_2 are converted to elemental sulfur. Tail gas from the sulfur recovery plant will be oxidized and recycled back through the adsorbers to remove any residual sulfur compounds.

High temperature sorbent exiting the regenerator is conveyed with an L-valve to the four-stage fluidized-bed sorbent cooler. The sorbent flows counter to the ambient air which cools the sorbent. Regenerated sorbent exits the cooler at 320°F. The sorbent is then conveyed through an L-valve to the sorbent surge tank before being returned to the adsorber, completing the sorbent cycle.

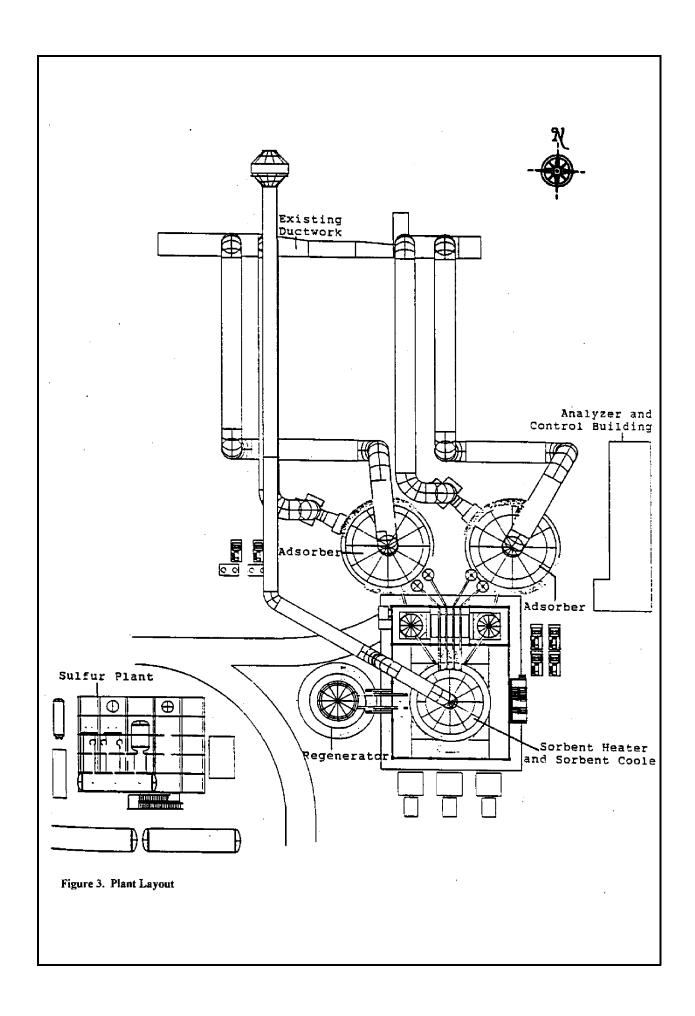
Ambient air which is forced through the sorbent cooler by the heater-cooler fans exits the sorbent cooler at approximately 950°F. This preheated air then enters the air heater where it is heated to approximately 1340°F. The high temperature air is used in the sorbent heater to heat the sorbent to the regeneration temperature of 1150°F.

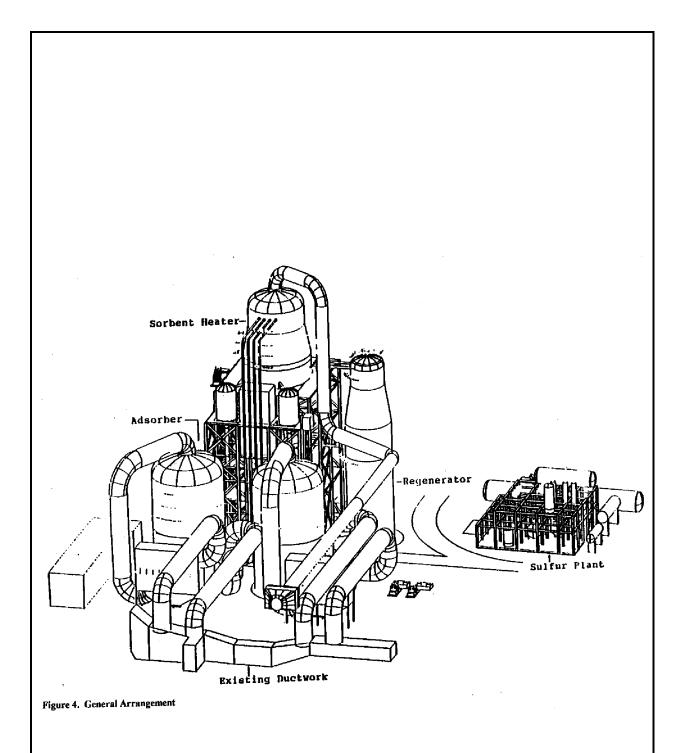
NOXSO Plant Description

The Demonstration Plant will be located in a generally unoccupied area of the plant yard south of Unit No. 2. This area requires minimal site preparation and provides adequate space for the NOXSO plant while offering a convenient tie-in point for the flue-gas ductwork, see Figure 3, since the existing flue-gas plenum and plant stacks are located on the south side of the power plant. This location also provides plant access from the south for sorbent and nitrogen delivery while the sulfur recovery unit is accessible by rail and road. The general arrangement is shown in Figure 4.

The NOXSO plant will take up an area approximately $250' \times 200'$ in size, just south of Precipitator Road, which is an east-west running plant access road south of the power plant. The analyzer and control building is located to the east of the NOXSO plant while the sulfur recovery unit is situated to the west, at the southern end of the battery limits.

The locations of the major process vessels within this area are chosen to minimize the amount of ductwork required to deliver and return the flue gas, and to minimize the horizontal distances that the sorbent must travel between vessels. Thus, the adsorption trains, including booster fans, adsorbers, and baghouses, are situated furthest north within the battery limits. The adsorption trains are shown in the foreground of Figure 4. The adsorbers, like the regenerator and sorbent cooler, are self-supporting vessels through the use of vessel skirts which reduce the overall amount of structural steel required.





The regeneration train, consisting of the sorbent heater, steam disengaging vessel, regenerator and sorbent cooler, is just south of the adsorption trains. The sorbent cooler and sorbent heater are in a stacked arrangement, so that the heat energy recovered by the fluidizing air in the sorbent cooler may be used in the sorbent heater. The sorbent cooler, hidden by the structural tower in Figure 4, is skirt supported on the ground, while the sorbent heater is supported 95' in the air at its base by the sorbent heater tower. This tower is centered behind and situated as close as possible to the two adsorbers to minimize the horizontal distance that the sorbent must travel between the two trains.

The regenerator and steam disengaging vessel are in a stacked arrangement to allow gravity flow of the sorbent between the two vessels. Again, to minimize the horizontal sorbent conveying distance, the regenerator is situated as close as possible to the sorbent heater tower. The regenerator is located on the west side of the tower because of space availability for the sulfur recovery unit, which is to the west of the regenerator. It is essential to position the sulfur recovery unit as close as possible to the regenerator to limit the distance of the steam-traced, regenerator off-gas line.

III. THE LIQUID SO₂ FACILITY

As discussed previously, the purpose of the NOXSO Clean Coal Project is to demonstrate the NOXSO flue-gas treatment system in a fully integrated commercial scale operation. The NOXSO plant will reduce SO_2 and NO_x emissions from Alcoa Generating Corporation's Warrick Power Plant Unit 2. The removed sulfur will be processed into elemental liquid sulfur. In addition, as part of the project, a liquid SO_2 plant has been constructed at Olin Corporation's Charleston, Tennessee facility to convert the sulfur into liquid SO_2 .

Host Site Information

Figure 5 is a site plan of the Olin Charleston Plant (OCP). There are five basic areas within the plant: administration, including process technology and product quality/environmental control buildings; chlor-alkali, consisting of chlorine/caustic soda production facilities, Reductone® (sodium hydrosulfite) production facilities, hydrochloric acid production facilities, boiler house, and water treatment; HTH® Dry Chlorinator (calcium hypochlorite) production facilities and associated warehousing; rubber services, and associated warehousing; and maintenance facilities.

As shown in Figure 6, OCP is located in Bradley County, in southeastern Tennessee about 12 miles northeast of Cleveland, Tennessee. Charleston, Tennessee, the closest town to the site, is 1.5 miles southeast of the plant. The OCP consists of roughly 975 acres between Lower River Road and the Hiwassee River (which flows to the northwest). Liquid SO₂ is a primary feedstock at the OCP where it is used to produce sodium hydrosulfite which is sold to the paper industry where it is used as a bleach for paper and clay.

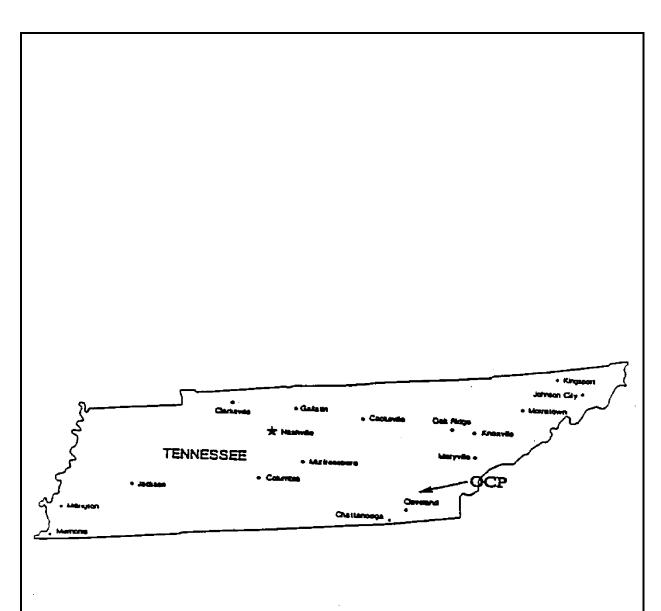


Figure 5. OCP Location

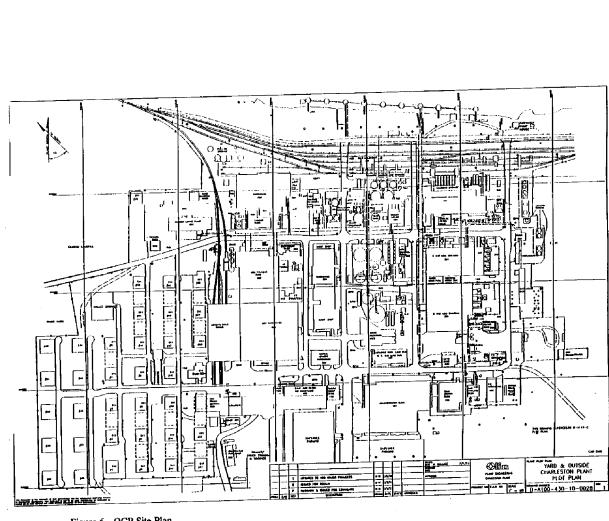


Figure 6. OCP Site Plan

Liquid SO₂ Process Description

The liquid SO_2 facility consists of two components, the liquid SO_2 plant and a cryogenic air separation plant. The facility is located on less than an acre of Olin property east of the existing switchgear building. Figure 7 presents the site plan for the liquid SO_2 facility detailing its relationship within Olin's plant site.

The SO_2 plant, the primary aspect of the liquid SO_2 facility, is an advanced liquid SO_2 production process designed for ease of operation and maintenance and to minimize process waste streams and emissions to the environment. Reliable operation of a 9,000 tpy commercial unit over the last five years has demonstrated and proven the technology. In the basic process, molten sulfur is oxidized to SO_2 vapor in compressed oxygen. The SO_2 vapor is then separated from vaporized sulfur and condensed. Key resources, including molten sulfur, oxygen (O_2) , and caustic, are fed to the process. The process in turn produces liquid SO_2 , steam, and sodium sulfite.

The cryogenic air separation plant provides 99.5% O_2 to the liquid SO_2 plant. The oxygen is produced by liquefying air and then using fractional distillation to separate it into its components. The air separation plant requires inputs of air, electricity, and cooling water and produces, in addition to the O_2 , a small amount of pure nitrogen (N_2).

Liquid SO₂ Plant Description

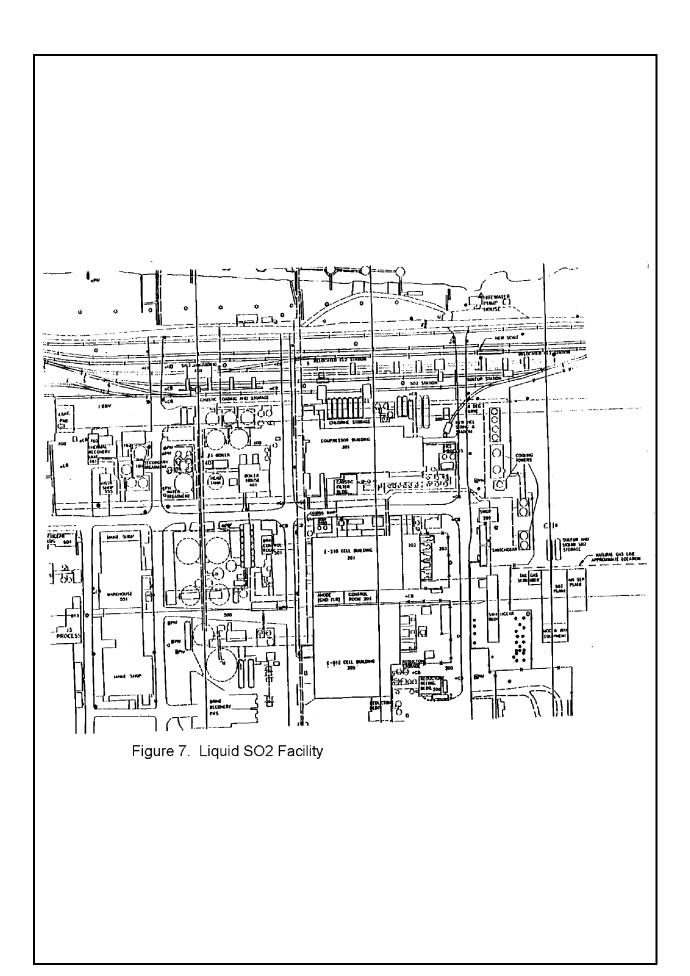
The facility will have the operating capacity to produce about 125 tpd (45,000 tpy) of liquid SO_2 . Figure 8 presents a basic flow diagram of the liquid SO_2 process. Primary unit operations are numerically labelled on this figure and referenced in the following discussion. Liquid sulfur at about 270°F is continuously pumped from two-250 ton capacity sulfur storage tanks (1) to the sulfur day tank (2). Sulfur flows by gravity from the day tank to the SO_2 reactor (3). The sulfur level in the reactor is controlled by equalization with the level in the sulfur day tank.

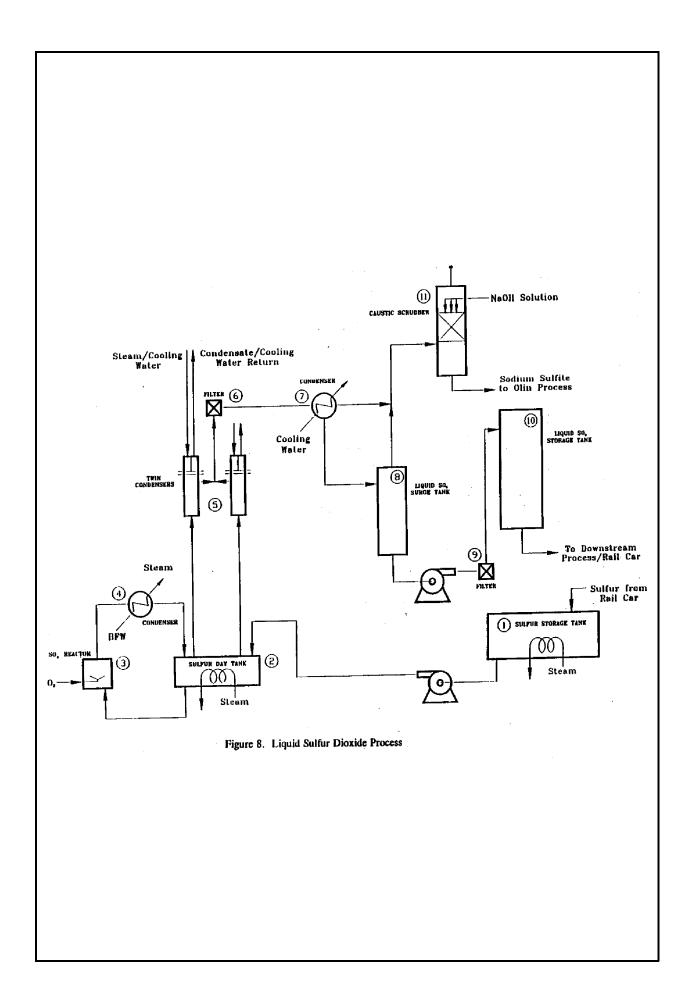
During start up the sulfur in the reactor is electrically heated to about 600°F. Oxygen is then injected into the sulfur through a submerged sparger. The sulfur at the reactor operating pressure, 80 psig and 600°F, is above the auto-ignition temperature. The following reaction occurs:

$$S + O_2 \rightarrow SO_2$$

The reaction is spontaneous and exothermic. The reactor temperature rises to about 1100° F, the boiling point of sulfur at 80 psig. The production rate of SO_2 is controlled by the oxygen feed rate to the reactor.

The vapor stream of SO_2 and sulfur is cooled in the sulfur condenser (4) to about $270^{\circ}F$. The condenser is cooled by generating steam at 35 psig. Most of the sulfur vapor condenses and the mixture of condensed sulfur, which flows by gravity, and SO_2 vapor is returned to the molten sulfur day tank. The liquid sulfur drops out in the sulfur day tank and is recycled to the reactor.





The SO_2 vapor does not condense at $270^{\circ}F$ and is not significantly soluble in molten sulfur. It is further cooled in the twin condensers (5) to remove additional trace amounts of sulfur. The condensers operate in a two step repeating cycle. In the first step, the condenser cools the SO_2 to $120^{\circ}F$ using cooling water. Entrained liquid sulfur and remaining sulfur vapor will collect as a solid on the condenser tube walls. In the second step, the condenser gas outlet is blocked and the sulfur is melted using low pressure steam. The molten sulfur will drain by gravity back to the sulfur day tank. The condensers will alternate between these modes of operation; one condenser will remove sulfur while the second condenser is regenerated using steam.

After filtration (6), the SO_2 vapor is condensed in the SO_2 condenser (7) using cooling water. At the system pressure of 80 psig, the SO_2 condenses at about 104°F. The liquid SO_2 will flow to the liquid SO_2 surge tank (8). From the surge tank it will be pumped through a filter (9) to remove any entrained particulate then to a 200-ton capacity liquid SO_2 storage tank (10). From the storage tank, the liquid SO_2 will be pumped to an existing process liquid SO_2 feed tank or to rail cars for shipment.

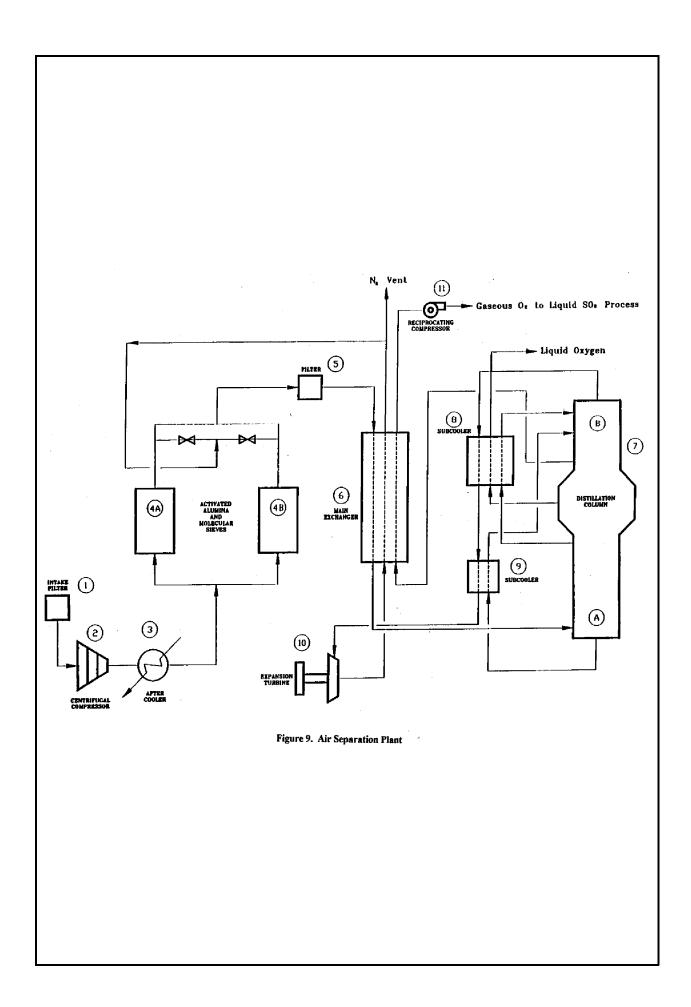
A vent stream from the SO_2 condenser and liquid SO_2 surge tank contains non-condensibles, trace amounts of nitrogen and argon introduced to the sulfur reactor with the oxygen, and SO_2 vapor. The SO_2 vapor is removed from the vent stream in a caustic scrubber (11). A sodium hydroxide (NaOH) solution is used to remove the SO_2 vapor from the gas stream. The sodium sulfite formed from the reaction of NaOH and SO_2 will be used by Olin to neutralize a chlorine waste stream from an existing Olin process.

Air Separation Plant Description

Figure 9 presents a basic flow diagram of the air separation plant used to supply O_2 to the liquid SO_2 process. Primary unit operations are numerically labelled on this figure and referenced in the following discussion. As mentioned previously, oxygen is produced by liquefying air and then using fractional distillation to separate the liquefied air into its components. The three fundamental steps in this process are purification, refrigeration, and rectification.

Purification

Atmospheric air contains dirt, water vapor, and carbon dioxide (CO₂) which must be removed from the compressed air stream to prevent plugging of downstream process equipment. The atmospheric air passes through an intake filter (1) to remove entrained particulate and is compressed to 125 psig in a centrifugal compressor (2). After compression the air is cooled in a direct contact after cooler (3) using cooling water. Carbon dioxide, water vapor, and gaseous hydrocarbons are then removed by adsorption on activated alumina and molecular sieve (4). Parallel units are used, like the twin condensers from the liquid SO₂ process, one bed will be regenerated while the other is online. The adsorbents are regenerated using heat and a nitrogen purge gas generated downstream.



Refrigeration/Rectification

The purified air passes through a pipeline filter (5) and enters the main exchanger (6) where it is cooled by heat exchange with outgoing gaseous oxygen and waste gas. After the main exchanger, the purified air enters the bottom section of the lower column (7A) of the distillation column (7). The lower column operates at about 60 psig while the upper column (7B) of the distillation column operates at about 5 psig. Rectification, vapor - liquid contacting, occurs in the distillation column. As the incoming air rises up the column, it contacts a descending liquid. Since oxygen has a higher boiling point than nitrogen, as the vapor ascends it becomes richer in nitrogen while as the liquid descends it becomes richer in oxygen. Cold nitrogen rich vapor is withdrawn from several places within the distillation column and used to cool recycle streams in the subcoolers (Units 8 & 9). Heat energy is also removed from the system by expanding the nitrogen rich vapor in the expansion turbine (Unit 10), thereby doing work and lowering the temperature. Pure oxygen vapor is withdrawn from the bottom of the upper column. This vapor is warmed in the main exchanger and compressed using a reciprocating compressor (11) to the required operating pressure.

Process Alternatives/Advantages

Traditional, older processes used to produce liquid SO₂ from sulfur involve burning the sulfur in air. The resulting gas stream can contain, at best, 16-18 vol.% SO₂ with the balance being mainly nitrogen, oxygen, and water from the combustion air. The SO₂ must then be separated from the other combustion gases. This is done by stripping the SO₂ from the gas stream using either water or an organic solvent like dimethylaniline. Regardless of which stripping liquor is used, these processes are more complex and have greater environmental impacts. To illustrate, the burn in air with water stripping process.

Process advantages of the burn-in-oxygen liquid SO₂ process include the following:

- Process gas at a lower temperature, 1100°F versus about 2500°F.
- Production of lower pressure steam, 35 psig versus 600 psig.
- No acidic wastewater stream which must be neutralized.
- Smaller volume tail gas stream which economically allows for the use of a more efficient scrubber resulting in lower SO₂ emissions.
- No spent acid stream which must be reclaimed or disposed of.
- No solvent emissions or disposal of solvent.

In addition, due to the lower process gas temperature and steam pressure, and simplicity of the process the liquid SO₂ process is inherently more reliable and safe to operate.

IV. ACKNOWLEDGEMENT

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